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Treatment of chlorinated volatile organic compounds in upflow wetland mesocosms

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Abstract

Sorption, biodegradation and hydraulic parameters were determined in the laboratory for two candidate soil substrate mixtures for construction of an upflow treatment wetland for volatile organic compounds (VOCs) at a Superfund site. The major parent contaminants in the groundwater at the Superfund site were *cis*-1,2-dichloroethene (*cis*-1,2-DCE) and 1,1,1-trichloroethane (1,1,1-TCA). The two mixtures—one a mixture of sand and peat, the other a mixture of sand, peat and Bion Soil, a product derived from agricultural wastes—were selected from ten possible mixtures based on the results of hydraulic and geotechnical testing. The sand and peat mixture had an average hydraulic conductivity of 4.95×10^{-4} cm/s with a critical flow of 39.5 gpm/acre (368 l/min/ha) without fluidization of the bed. The sand, peat and Bion Soil mixture had an average hydraulic conductivity of 3.02×10^{-4} cm/s with a critical flow of 36.8 gpm/acre (344 l/min/ha) without fluidization of the bed. Retardation coefficients ranged from 1 to 7.3 for target VOCs with higher coefficents observed in the mixture containing the Bion Soil. Consistently higher spatial and temporal first-order removal rate constants were observed in the sand, peat and Bion Soil mixture (*cis*-1,2-DCE, 0.84 ± 0.36/day; 1,1,1-TCA, 6.52 ± 3.12/day) than in the sand and peat mixture (*cis*-1,2-DCE, 0.37 ± 0.13/day; 1,1,1-TCA, 1.48 ± 0.42/day). Results from anaerobic microcosm studies confirmed that biodegradation was occurring in the columns and that the sand, peat and Bion Soil mixture had higher degradation rate than the sand and peat mixture. Vinyl chloride (VC) was identified as a 'design' contaminant since it is a proven carcinogen and had the lowest removal rate constant for both substrate mixtures. Effective wetland bed depths for VC removal of 900 and 210 cm will be required for peat and sand alone and sand, peat and Bion Soil mixtures, respectively.
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1. Introduction

Chlorinated volatile organic compounds (VOCs) are suspected carcinogens that are common groundwater pollutants and pose special treatment problems (Wiedemeier et al., 1996).

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Natural treatment systems including treatment wetlands may provide a cost-effective alternative for contaminated groundwater, either by intercepting groundwater plumes or by serving as treatment for pumped groundwater (Pardue et al., 2000). Removal of VOCs has been shown to be remarkably fast in natural peat wetlands bordering the Aberdeen Proving Grounds, MD (Lorah et al., 1997; Lorah and Olsen, 1999a,b). Attenuation of high concentration of trichloroethene (TCE) and 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA) has been observed as groundwater flows through the base of these marshes and then upward to the surface. Important fate mechanisms include sorption of VOCs onto peat, reductive dechlorination of VOCs by microorganisms in the anaerobic portion of the marsh and cometabolism of chlorinated VOCs by methanotrophic bacteria in aerobic portions of the marsh (the root rhizosphere) (Lorah et al., 1997). The efficiency of these reactions suggests that an upflow treatment wetland could be designed to mimic behavior of these natural systems. A preliminary design approach for treatment wetlands for VOCs has been published (Pardue et al., 2000).

In a treatment wetland system for VOCs, contaminated groundwater would be pumped into the wetland bed in an upflow mode to minimize volatilization. Chlorinated organics in the groundwater plume would be applied to the base of the wetland where conditions are anaerobic. Under these conditions, reductive dechlorination of chlorinated VOCs is possible. Efficient reductive dechlorination has been observed in wetland soils for a number of contaminants (Parsons et al., 1984; Parsons and Barrio-Lage, 1985; Barrio-Lage et al., 1986; Pardue et al., 1996; Jackson and Pardue, 1998; Lorah et al., 1997; Lorah and Olsen, 1999a,b). As the water moved upwards, sorption of VOCs onto the highly organic soil would retard the movement of the compounds resulting in longer detention times (Lorah et al., 1997). Within the plant root zone, the lower chlorinated daughter products would pass through a high surface area rhizosphere populated by methanotrophic bacteria (King, 1994; Calhoun and King, 1997). At Aberdeen Proving Ground, microcosm studies indicated

that daughter and remaining parent products could be degraded to CO_2 via this process (Lorah and Olsen, 1999a). Plant uptake would act in a complementary way to remove any remaining parent or daughter compounds (Burken and Schnoor, 1998). The mass of target organics would decrease as the water moves closer to the surface. Very low concentrations of chlorinated organics should reach the surface, thus presenting little risk to wetland biota.

Before embarking on a full-scale treatment wetland, it was necessary to conduct bench-scale studies to investigate the feasibility of using constructed wetlands for treatment of VOCs. The overall objective of the bench-scale studies was to provide information for establishing the feasibility of a pilot-scale treatment wetland for a Superfund site in Connecticut. The specific objectives of the study were as follows: (1) to assess the hydrodynamics of VOC-contaminated water flowing through peat beds in a wetland mesocosm, (2) to measure sorption potential of candidate peats, (3) to measure degradation potential of target compounds in candidate peat substrate mixtures in a bench-scale treatment wetland, (4) to correlate degradation in bench-scale wetlands with natural attenuation parameters, and (5) to confirm evidence of biodegradation processes observed in the bench-scale soil columns and to examine transformation patterns of representative chlorinated ethanes and ethenes using anaerobic microcosms.

2. Methods

2.1. Candidate substrate mix selection approach

Ten substrate mixtures were prepared for hydraulic conductivity measurements based on the results of previous geotechnical testing (dry bulk density, moisture content, organic carbon content, grain size analysis, and pH). The objective of this testing was to evaluate which materials would be suitable for bench-scale studies. Results of hydraulic conductivity tests were used to select two substrate mixtures for measurement of sorption and degradation potentials of target compounds in a bench-scale treatment wetland.

Geotechnical testing was performed on the four basic candidate substrates *Bion Soil* (Dream Maker Dairy, Cowlesville, NY), a product derived from agricultural waste; and three commercially available peats: *Premier* (Premier Horticulture Ltd, Dorval, Que., Canada), *Latimer* (Latimer's Peat Moss Farm, West Liberty, OH) and *Worcester* (Worcester Peat Co. Inc., Cherryfield, ME). Hydraulic conductivity was determined using the falling head method (Charbeneau, 2000). Table 1 presents a summary of geotechnical characteristics of the tested substrates.

Each substrate was tested separately to provide a better understanding of material's characteristics under saturated conditions (Mixes 1, 3, and 5). Each substrate was also tested following an addition of sand to measure the corresponding effect on the material's permeability (Mixes 2, 4, and 6). Fine to medium sand was used for preparing the mixtures. Four additional mixes (7 through 10) were developed based on the following general criteria: (1) the overall mix should result in a volume-averaged density greater than 62.4 per cubic foot (pcf) (1 kg/l) and preferably above 75 pcf (1.2 kg/l) (to prevent flotation of the material in water and to withstand an induced upward hydraulic gradient), (2) the overall mass-averaged total organic content (TOC) should be greater than 20% and preferably nearing 50% (typical organic carbon content of a mature wetland peat) suitable for significant microbial activity; and (3) the overall mass-averaged pH should be in the neutral range near pH 7. The composition and rationale for each mixture is presented in Table 2.

2.2. Sorption isotherms

Sorption experiments were done using 40 ml VOA vials (ICHEM) containing the Superfund site water, sodium azide as a biocide, and 12 g (dry weight) of peat. Except for TCE no other VOC was added to the site water prior to sorption studies. Six points of the isotherm were developed across the range of water concentrations of VOCs. Isotherm points were generated by diluting the site water with an electrolyte solution (0.01 M $CaCl_2$) using dilutions of 1:1, 1:2, 1:5, 1:10 and 1:20. Three replicate vials were used for each isotherm point for a total of 18 vials. Simultaneous measurement of partitioning of TCE, *cis*-1,2-dichloroethene (*cis*-1,2-DCE), 1,1,1-TCA and 1,1-dichloroethane (1,1-DCA) was performed. Samples were shaken on a reciprocating shaker at 20 °C for 48 h, centrifuged, and the supernatant analyzed for target compounds using EPA Method 8260B, as described below.

2.3. Bench-scale wetland apparatus

Column experiments were performed in three 60 cm long, 15 cm diameter glass columns with 5 sampling ports equipped with Mininert Valves (VICI Precision Sampling, Baton Rouge, LA) along their lengths (Fig. 1). Soil column apparatus and accessories were made from Viton, Teflon, stainless steel, and glass to avoid adsorption of VOCs. The experiment was set-up in a temperature controlled greenhouse at 26±3 °C. Three mesocosms were constructed, two with the candidate peats (Mix 4, a combination of Latimer peat and sand, and Mix 7, a combination of Latimer

Table 1
Summary of substrate characteristics

Parameter	Bion Soil	Latimer	Premier	Worcester	Sand (estimated)
Saturated density at 5 psi surcharge (pcf)	34.6	8.9	14.2	8.3	100
TOC (%)	57.1	82.5	96.5	99.6	0
pH	7.4	2.9	5.3	2.9	7
D_{10} (mm)	0.002	0.15	0.15	0.1	0.1
Saturated moisture content (%)	125.4	602.4	349.3	591.8	–
Saturated unit weight (pcf)	78	66	63.8	57.4	120

One pound per cubic feet (pcf) = 0.016 kg/l.

Table 2
Summary of selected substrate mixtures and rationale

Mix	Bion Soil[a] (%)	Latimer[a] (%)	Premier[a] (%)	Sand[a] (%)	Rationale
1	100	–	–	–	Determine permeability of *Bion Soil*
2	80	–	–	20	Evaluate the potential effect of adding sand on *Bion Soil* permeability
3	–	100	–	–	Determine permeability of *Latimer*
4	–	80	–	20	Evaluate the potential effect of adding sand on *Latimer* permeability
5	–	–	100	–	Determine permeability of *Premier*
6	–	–	80	20	Evaluate the potential effect of adding sand on *Premier* permeability
7	40	40	–	20	Evaluate permeability of the *Bion Soil* and *Latimer* mix
8	40	–	40	20	Evaluate permeability of the *Bion Soil* and *Premier* mix
9	70	–	30	–	Evaluate permeability of *Bion Soil* with Premier amendment for increased TOC
10	70	30	–	–	Evaluate permeability of *Bion Soil* with Latimer amendment for increased TOC

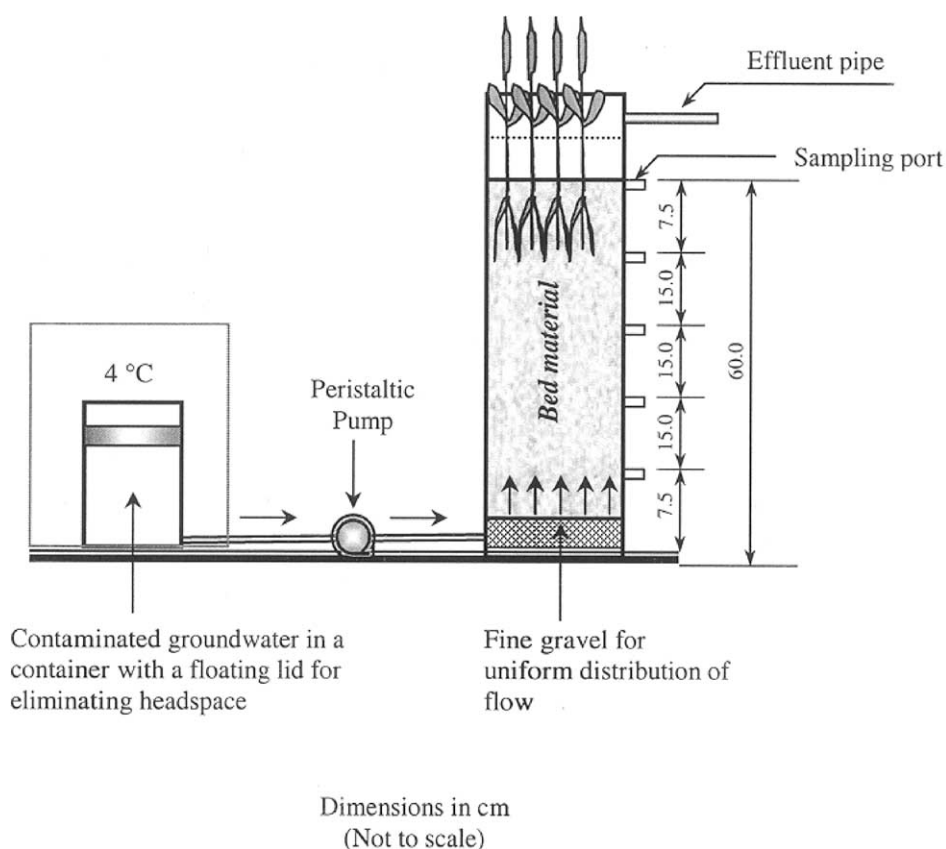[a] All values are percent by volume.

Fig. 1. Schematic diagram of the bench-scale wetland treatment system.

peat, sand and Bion Soil) and one with a clean autoclaved sand. The sand column was used as a reference column since neither sorption nor degradation of VOCs was expected to occur in the column primarily due to the absence of organic matter. The mesocosms were glass cores packed to a uniform bulk density. Column and flow characteristics are shown in Table 3. A 1-cm layer of fine gravel was placed at the bottom for even distribution of flow through the column. Mix 4 and Mix 7 columns were planted with 5 young *Scirpus americanus* shoots approximately 6 inches in length. To avoid introducing organic matter, the sand column was not planted. Glass wool was inserted in the inner side of sampling ports to minimize dead zones and clogging of sampling ports. The sides of the columns were wrapped with aluminum foil to keep off light for minimization of growth of photosynthetic organisms. Ground-

water from a Superfund site contaminated with chlorinated ethenes and chlorinated ethanes was introduced through 2-mm i.d. stainless steel tubing in an upflow mode. Contaminated groundwater was shipped from the site on a weekly basis under refrigerated conditions to minimize losses of VOCs during transportation. The water was neither treated nor contaminants added prior to introduction into the columns.

The peat columns were fully saturated and flooded to a depth of 10 cm. A pump (Cole Parmer Model No. 7523-40) with Viton tubing was used to convey the site groundwater through the column. Headloss (based on pressure differences between the bottom and top of the core) and the actual flow rate were measured every 7 days in the peat cores. These measurements were used to estimate pore velocity and calibrate a mass transport equation to describe system performance. Actual flow rates were determined by measuring the volume of water applied to each core in a specified duration of time.

Influent solutions were refrigerated throughout the experiment at about 4 °C to minimize volatilization. In addition, a floating cap was used to prevent the development of a headspace in the bottle. The influent concentrations were monitored three times a week to ensure that changes in concentration were minimal. Influent samples for all column experiments were collected from the delivery side of the pump. Samples for analysis of chlorinated VOCs were collected by withdrawing porewater from the axial center of the soil columns with a prerinsed gastight 10 ml Hamilton glass syringe fitted with luer-lock and injected into 2 ml glass vials with liquid facing Teflon lined caps. Six samples were taken for each core, one from the inlet tube, one from 5 sampling ports located along the length of the columns (Fig. 1), and one sample from the effluent (5 cm below the standing water level on top of the core). Sampling of the ports for the first 3 months was performed at 7 days intervals, thereafter the sampling interval was increased to between 2 and 3 weeks. The column experiments were run continuously for 320 days with brief periods of interruptions during maintenance of the soil column systems.

Table 3
Physical characteristics of columns and flow data

Characteristics/parameters	Soil column		
	Mix 4	Mix 7	Sand
Column characteristics			
Length (cm)	60	60	60
Diameter (i.d.) (cm)	15	15	15
Total volume (V_T) (cm^3)	10 603	10 603	10 603
Bulk density, (ρ_b) (g/cm^3)	1.20	1.25	1.65
Media density (ρ) (g/cm^3)	0.34 ± 0.09	0.57 ± 0.04	1.260[a]
Media total mass (g)	3605	6044	13 413
Media porosity (ε) (cm^3/cm^3)	0.76 ± 0.04	0.72 ± 0.06	0.38[a]
Pore volume (V_p) (cm^3)	8058	7634	4029
Flow data			
Pore velocity (u_p) (cm/s)	1.87 × 10^{-4}	1.83 × 10^{-4}	1.78 × 10^{-3}
Hydraulic residence time (τ)[b] (day)	9.3	9.1	4.6
Measured flow rate Q (cm^3/min)	0.60 ± 0.09	0.58 ± 0.12	0.61 ± 0.21
Hydraulic conductivity (k) (cm/s)	4.95 × 10^{-4}	1.3 × 10^{-4}	1.4 × 10^{-2}

[a] Typical value for medium sand (Bouwer, 1978; Kasenow, 1997).
[b] Hydraulic residence time; $\tau = V_p/Q$.

2.4. Anaerobic microcosm experiments

Following the conclusion of the mesocosms studies, the Latimer peat and sand mixture (Mix 4) and the Latimer peat, sand and Bion Soil mixture (Mix 7) soil were removed from the glass cores minimizing disturbance. The bottom 10 cm of each core was sectioned and used to construct anaerobic microcosms. The bottom section was selected for construction of microcosms because more than 50% of all contaminants were removed within 10 cm from the core bottom in both Mix 4 and Mix 7 soil columns.

Construction of anaerobic microcosms was done under a nitrogen atmosphere in a glove-bag by homogenizing and placing soil in 160 ml serum bottles using a 1.5:1 volumetric ratio of groundwater to wetland soil (Lorah et al., 1997). All reaction mixtures were sealed with Teflon-lined rubber septa and aluminum crimp seals and incubated in an inverted position under static conditions at 25 °C in the dark, which was the approximate temperature of the groundwater during the soil column experiments. Resazurin (0.0002%) was added as a redox indicator. Three replicates were prepared for each treatment. Initially, groundwater contaminated primarily with *cis*-1,2-DCE and 1,1,1-TCA from the Superfund site was used for the experiments. After all the contaminants were reduced to below detection, one compound representative of chlorinated ethanes (1,2-dichloroethane (1,2-DCA)) and one representative of chloroethenes (1,2-*cis*-DCE) were selected for further investigation of transformation kinetics and biodegradation routes. Although 1,2-DCA was not one of the prominent contaminants, the chemical was however, chosen because of it can dechlorinate via hydrogenolysis and dichloroelimination mechanisms. *cis*-1,2-DCE and 1,2-DCA at a concentration of about 5 mg/l were consecutively spiked three times into each microcosm for a total of nine runs per treatment. This was done to further determine degradation patterns and mechanisms of biodegradation of the contaminants. Temporal monitoring of concentrations of parent compounds and daughter products was done after each spike until the concentrations of the contaminants dropped below the analytical method detection limit. Stock solutions of *cis*-1,2-DCE and 1,2-DCA were made from neat chemicals and added to the microcosms using gas-tight syringes to give the planned initial dissolved concentrations. Sterile controls were included in the study to monitor for non-biological losses of the test chemicals. Microcosms were prepared as described above, and were adjusted to contain 1% formalin.

Samples were withdrawn from the bottles and immediately analyzed without storage for chlorinated ethenes and ethanes, ethene, ethane and methane at intervals ranging from 6 to 24 h. Biodegradation rates were calculated by a first-order approximation. When significant losses ($> 5\%$) were observed in the sterile microcosms, these losses were subtracted from the concentration in the non-sterile microcosms before the first-order rate constant was calculated (Lorah et al., 1997).

2.5. Analytical procedures

VOCs were analyzed using EPA Method 8260B using a purge and trap apparatus to concentrate and introduce the sample onto the gas chromatograph-mass selective detector (Agilent 6890 gas chromatograph-5972A mass selective detector). Daily blanks, calibration checks and tunes were run to assure that the analytical method was in control. Recovery of dibromofluoromethane (Supelco Inc., Bellefonte, PA) surrogate injected into every sample also ensured that no gross dilution errors or leaks occurred in the GC-MS system.

Porewater (25 ml) from the wetland cores was collected using a gastight Hamilton syringe for analysis of methane, ethene, and ethane. The water was transferred to a 25 ml glass vial fitted with a liquid facing Teflon cap. A headspace was created (10 ml) by displacing water using ultra pure nitrogen with a gastight syringe. The vial was heated using a hot plate at a temperature of 90 °C to establish equilibrium. Henry's Law constants are well known at these higher temperatures. Methane, ethene and ethane in porewater were measured using GC-FID. A subsample (3 ml) of gas in the headspace was withdrawn using a gastight syringe and injected into the GC-FID

(Agilent 5890 Series II) equipped with a 2.4 m × 0.32 mm ID column packed with Carbopack B/1% SP-1000 (Supelco Inc.). The column temperature was held at 40 °C isothermally for 6.5 min, and the injector and detector temperatures were 375 and 325 °C, respectively. The carrier gas was ultra high purity nitrogen at a flow rate of 12 ml/min.

Measurement of temperature, pH, conductivity, oxidation–reduction potential (ORP), total dissolved solids, dissolved oxygen and conductivity was performed using a multimeter (Ultrameter by Myron L Company, Carlsbad, CA). Spectrophotometric methods were attempted for measurement of nitrite, nitrate, ferrous iron, ferric iron, chloride, sulfate and sulfide but suffered from the small volumes of water available. Hydrogen was analyzed using a reduction gas analyzer (RGA-5, Trace Analytical, Palo Alto, CA). Organic acids (lactate, formate, succinate, acetate, propionate, butyrate and benzoate) were analyzed using high-pressure liquid chromatograph (HP 1090 Series II Liquid Chromatograph).

Analysis of dissolved gaseous constituents (ethene, ethane, methane, hydrogen and oxygen), temperature, pH, conductivity, ORP, total dissolved solids, and conductivity required withdrawals of large volumes (> 25 ml) of porewater, which would have substantially changed the spatial distribution of the VOCs. Due to this sample volume limitation, composite samples had to be strategically collected instead of sampling from each port. Two composite samples were collected by withdrawing 8 ml of porewater from each of the top two and bottom three sampling ports, representing the 'root zone' and 'below root zone' sections of the cores, respectively.

2.6. Chemicals

Analytical standards and surrogate for the VOCs were obtained as mixtures or neat liquids from Supelco Inc. Methane, ethane and ethene calibration gases were obtained from Gas Products (Baton Rouge, LA). Other chemicals used in this study were reagent grade and were purchased from various vendors.

2.7. Data modeling

The potential for fluidization of the wetland bed was evaluated as part of the design analysis. Fluidization may result in short-circuiting of water from the bottom distribution layer to the wetland surface and if sufficiently severe, potentially result in failure of the treatment wetland. Fluidization occurs when the difference in pressure forces between the lower and the upper layers exceed the gravitational force of the substrate mass. Under such conditions, the effective stress through the substrate will effectively become zero and fluidization may occur. The potential for fluidization was evaluated by considering the effective stress within the substrate bed and estimating the maximum flow rate to prevent fluidization. Effective stress, the portion of the total stress carried by the pore water, maintains peat stability. The reduction of effective stress resulting from upward seepage can be calculated as:

$$\sigma = z(\gamma_{sat} - \gamma_w) - iz\gamma_w \qquad (1)$$

where z [L] is the depth of the substrate bed, γ_{sat} (M/L^3) is saturated unit weight of the substrate, γ_w [M/L^3] is unit weight of water, σ [M/L^2] is the effective stress and i [L/L] is the hydraulic gradient. A critical gradient, i_{cr} [L/L] can be defined by setting the effective stress equal to zero. This results in:

$$i_{cr} = \frac{\gamma_{sat} - \gamma_w}{\gamma_w} \qquad (2)$$

Critical flow per unit surface area of the wetland, q_{cr} [L/T] is calculated as follows:

$$q_{cr} = ki_{cr} \qquad (3)$$

where k [L/T] is the hydraulic conductivity of the wetland bed substrate.

The sorption distribution coefficient K_d [L^3/M] in a linear sorption model can be described by

$$K_d = q_e/C_e \qquad (4)$$

where q_e is the mass of chemical sorbed per unit mass of soil [M/M] and C_e [M/L^3] is the equilibrium concentration. Nonlinear isotherms can be described by the Freundlich equation

$$q_e = K_F C_e^N \tag{5}$$

where K_F [L^3/M] is the Freundlich sorption constant and N is the Freundlich exponent.

The organic carbon content normalized distribution coefficient K_{oc} [L^3/M] is described by

$$K_{oc} = K_d/f_{oc} \tag{6}$$

where f_{oc} is the fraction organic carbon content of the sample.

The linear partition coefficient of a compound $K_p(VOC)$, can be calculated from known linear partition coefficient of another compound $K_p(known)$, using the rearranged form of the classic Karickhoff relationship (Karickhoff, 1981):

$$K_p(VOC) = \frac{K_p(known)K_{ow}(VOC)}{K_{ow}(known)} \tag{7}$$

where K_{ow} [L^3/M] is the octanol–water partition coefficient.

A mass transport model was used to describe the movement of VOCs through the bed. The model is based on the following 1-D lumped first order kinetic reaction equation:

$$C = C_o e^{-kRx/v} \tag{8}$$

where C [M/L^3] is the concentration of the pollutant at a vertical distance, x [L], C_o [M/L^3] is the initial concentration, k [1/T] is a lumped temporal removal rate constant, R is the retardation coefficient (unitless) and v [L/T] is the seepage velocity.

The retardation coefficient R is calculated as follows

$$R = \left(1 + \frac{\rho_p}{\eta}K_d\right) \tag{9}$$

where ρ_p [M/L^3] is the bulk density of the medium, η is the porosity, K_d [L^3/M] is the linear distribution coefficient.

The mass transport model (Eq. (8)) assumes that the effect of molecular diffusion/dispersion on contaminant transport is insignificant, a reasonable assumption for homogenous medium; that a degradation rate constant is available that integrates the biodegradation occurring in the aqueous and sorbed phases; and the system is at steady state.

The spatial lumped removal rate constant k_s [1/L] can be calculated from the first–order kinetic reaction,

$$C = C_o e^{-k_s x} \tag{10}$$

Other parameters have been defined above. It is worth noting that for a given contaminant, the spatial degradation rate constant does not account for sorptive and hydraulic properties of the substrate.

Modeling of *cis*-1,2-DCE and vinyl chloride (VC) monitoring data in anaerobic microcosms was done using pseudo sequential dechlorination first-order kinetic models,

$$\text{First step: } [DCE]_t = [DCE]_o e^{-k_1^t} \tag{11}$$

$$\text{Second step: } [VC]_t = \frac{k_1[DCE]_o}{(k_2 - k_2)}(e^{-k_1^t} - e^{-k_2^t}) \tag{12}$$

where $[DCE]_t$ [M/L^3] is the concentration of *cis*-1,2-DCE at any time t; $[DCE]_o$ [M/L^3] is the initial concentration of *cis*-1,2-DCE; $[VC]_t$ [M/L^3] is the concentration of VC at any time t,; k_1 [1/T] and k_2 [1/T] are the pseudo first-order reaction rate constants for *cis*-1,2-DCE and VC degradation, respectively.

3. Results and discussion

3.1. Hydraulic characteristics

Table 4 summarizes the hydraulic conductivity results and computes critical flows achievable without causing fluidization. Based on critical flow values presented in Table 4, Mix 4 (Latimer peat and sand mixture) and Mix 7 (Latimer peat, Bion Soil and sand) were selected as the most promising substrate mixtures for construction of the wetland bed. These mixtures were selected because they had the highest critical flow, implying that they are least prone to fluidization. Mixture 4 had an average hydraulic conductivity of 4.95×10^{-4} cm/s with a critical flow of 39.5 gpm/acre (368 l/min/ha). Mix 7 had an average hydraulic conductivity of 3.02×10^{-4} cm/s with a critical flow of 36.8 gpm/acre (344 l/min/ha). Therefore, sorption and column experiments were conducted

Table 4
Summary results of hydraulic conductivity tests

Mix	Composition				Volume averaged saturated bulk density	Submerged unit weight[a]	Critical hydraulic gradient[b]	Mass averaged TOC	Mass averaged pH	Hydraulic conductivity average	Critical flow[c]	Critical flow/S.F. = 1.5
	Bion (%)	Latimer (%)	Premier (%)	Sand (%)	(pcf)	(pcf)	(ft/ft)	(%)	(S.U.)	(cm/s)	(gpm/ acre)	(gpm/acre)
1	100				78	15.6	0.25	57.1	7.4	1.99E−05	3.20	2.13
2	80			20	86.4	24	0.38	33.1	7.2	2.17E−05	5.32	3.55
3		100			62.5	0.1	0.002	82.5	2.9	1.43E−04	0.147	0.10
4		80		20	74	11.6	0.19	21.7	5.9	4.95E−04	59.03	39.4
5			100		63.8	1.4	0.02	96.5	5.3	2.96E−05	0.43	0.28
6			80	20	75	12.6	0.20	35	6.4	3.68E−05	4.76	3.17
7	40	40		20	80.2	17.8	0.29	29	6.8	3.01E−04	55.19	36.8
8	40		40	20	80.7	18.3	0.29	33.9	6.9	5.68E−05	10.68	7.12
9	70		30		73.5	11.1	0.18	63	7.1	4.72E−06	0.53	0.36
10	70	30			73.3	10.9	0.17	59.6	7	9.37E−06	1.05	0.70

Notes: S.F., safety factor; 1 pcf = 0.016 kg/l; 1 gpm/acre = 9.35 l/min/ha.

[a] Submerged unit weight calculated as Saturated Density − Water Density = D_{sat} − 62.4 pcf.

[b] Critical hydraulic gradient = $(D_{sat} - D_{water})/D_{water}$ = $D_{submerged}/62.4$ pcf.

[c] Critical flow = (Average hydraulic conductivity (cm/s)) × (Critical hydraulic gradient (cm/cm)) × (641395.28 gpm/acre) × (1 acre).

for these mixes to determine their sorptive and chlorinated solvent degradation capabilities.

Peat materials in general have low bulk density and hydraulic conductivity (as low as 1.06×10^{-7} cm/s) (Lorah et al., 1997). Densities less than that of water are not uncommon for peat materials, e.g. *Worcester*, one of the peat materials used in this study had a saturated bulk density of 0.92 kg/l. Low hydraulic conductivity will allow unreasonably low flows to pass through the wetland bed and peat material with saturated density lower than that of water will have a negative critical flow according to Eq. (1) and will, therefore, float on water. For these reasons, peat materials were mixed with sand to increase their bulk densities and hydraulic properties. For example mixing Latimer peat (80% V/V) and sand (20% V/V) increased the bulk density and hydraulic conductivity of the original peat material by a factor of 1.2 and 3.5, respectively. The resulting organic carbon content of the mixtures was lower than that of 'pure' materials by factors ranging between 1.7 and 3. However, the values of organic matter content of the mixtures were generally comparable to those of mature wetland peat ($>20\%$) as Table 4 shows.

3.2. Sorption and retardation

Batch adsorption experiments were performed using the selected substrate mixtures (Mix 4 and Mix 7) as sorbents to determine the potential for retardation of the contaminants in the wetland soil columns. Isotherm data were fit by both a Freundlich model (Eq. (5)) and a linear partitioning model (Eq. (4)). Table 5 summarizes results of sorption experiments for the substrate mixtures. The Karickhoff relationship (Eq. (7)) was utilized to predict the partitioning of VC due to its low concentration in the site groundwater. Both the linear and Freundlich models fit the data well ($r^2 > 0.85$). Based on these fits, there does not appear to be any reason to select the more complex, 2-parameter Freundlich model. Partition coefficients of all contaminants for Mix 7 (peat, sand and Bion Soil) were significantly higher than

those for Mix 4 (peat and sand alone). This is attributed to the effect of the organic Bion Soil. Surprisingly organic carbon content normalized distribution coefficients of some pollutants (notably 1,1-DCA and *cis*-1,2-DCE) for Mix 7 are also appreciably higher than those of Mix 4 (Table 5). The nature of organic matter has been reported to play a significant role in the sorptive behaviors of sediments. Therefore, differences in the quality of organic matter apart from organic matter content could account for the observed differences in sorption potential of the investigated substrate mixtures (Rutherford et al., 1992; Karapanagioti and Sabatini, 1997; Werth and Reinhard, 1997). Based on parameter values (K_p, K_F and K_{oc}) for both models, the results demonstrate that Mix 7 had a higher sorption capability for all contaminants than Mix 4.

Retardation coefficients of the contaminants for VOCs in the substrate mixtures range from slightly above 1 to approximately 7 (Table 5). Computed retardation coefficients for target VOCs are very similar to those reported by Lorah et al. (1997) from 'natural' Canal Creek wetland peat (R's ranging from 6 to 10) from Aberdeen Proving Ground, MD. From Table 5 it can be observed that Mix 7 has significantly higher retardation coefficients than Mix 4 for all contaminants.

3.3. Fate of VOCs in mesocosms

In general, two groups of compounds were detected in the site groundwater, chlorinated ethenes (*cis*-1,2-DCE and VC) and chlorinated ethanes (1,1,1-TCA, 1,1-DCA, and chloroethane (CA)). TCE (a parent compound of *cis*-1,2-DCE and VC) was below the detection limit (10 µg/l at this dilution) in the site water. These five compounds represent the bulk of the chlorinated compounds detected. Results were somewhat skewed by differences in the influent concentrations from the batches of groundwater from the site. This is illustrated in profiles of concentrations measured in the sand core (Fig. 2). It is expected that this variability is a natural result of the extraction process at the wells and will also be a factor in a pilot and full-scale treatment wetland systems. Observations of VOCs fate in the cores

Table 5
Summary of sorption results and retardation coefficients of contaminants

Compound	Sorption isotherm models						R^b
	Linear		Freundlich				
	Parameter values		Parameter values				
	K_p and K_{oc}^a (l/kg)	r^2	K_F(l/kg)	N	r^2		
Mix 7							
cis-1,2 dichloroethene	8.02 (27.66)	0.948	10.69	0.88	0.953		7.32
TCE	4.62 (15.93)	0.911	10.97	0.56	0.963		4.64
1,1-DCA	4.67 (16.10)	0.850	4.27	0.68	0.900		4.68
Chloroethane[c]	3.32 (11.45)	–	–	–	–		3.62
1,1,1-trichloroethane	7.06 (24.34)	0.997	7.34	0.92	0.996		6.56
VC[c]	0.26 (0.89)	–	–	–	–		1.20
Mix 4							
cis-1,2 dichloroethene	4.13 (19.03)	0.940	7.71	0.76	0.952		3.51
TCE	2.88 (13.27)	0.932	5.71	0.66	0.950		2.75
1,1-DCA	1.34 (6.18)	0.850	1.26	0.69	0.891		1.81
Chloroethane[c]	1.00 (4.61)	–	–	–	–		1.40
1,1,1-trichloroethane	4.43 (20.41)	0.974	4.43	1.00	0.974		3.69
VC[c]	0.11 (0.51)	–	–	–	–		1.07

[a] Organic carbon content normalized distribution coefficients (K_{oc}) are shown in brackets.

[b] Calculated using Eq. (9).

[c] Partition coefficient computed using Karickhoff relationship.

are grouped into two time periods: a start-up period during the first 10–12 weeks where concentrations throughout the core were variable and a period of apparent equilibrium after 10–12 weeks. The entire monitoring period spanned 45 weeks.

Concentrations observed up to a distance of 37.5 cm from the core bottom in the sand core were very similar to influent concentrations (Fig. 2). Decreases in concentrations of the contaminants in the top 22.5 cm of the sand column were probably due to direct volatilization losses due to the highly permeable nature of sand. Low or negligible concentrations were measured at the effluent (standing water at the top of the core) in the sand column indicating how rapidly volatilization can remove those compounds that arrive at the surface. Measuring VOCs concentrations in the standing water at the wetland surface would be a poor indicator of performance since similar concentrations were measured in both peat and sand cores. Degradation daughter products of the VOCs were not detected in the sand column. The

above observations indicate that negligible biodegradation and little sorption was occurring in the sand column, as expected. Since concentrations were very similar to influent concentrations (at least up to a distance of 37.5 cm), the lack of bias in the sampling procedures was also demonstrated.

The distribution of *cis*-1,2-DCE and CA in the core containing Mix 4 (Latimer peat and sand) is shown in Fig. 3. After the ninth week, decreases in concentrations were observed in the column containing Mix 4 that were attributed to biodegradation, as observed from the sharp drop in *cis*-1,2-DCE (Fig. 3). This was after the initial contaminant 'front' had passed through much of the column. Subsequent measurement of *cis*-1,2-DCE in this core were low (< 1 mg/l) above the midpoint of the core despite similar influent concentrations. Increased VC along the flow path was also detected during this period as Fig. 4 shows. CA concentrations also showed decreases in concentration (Fig. 3) that were not expected from sorption alone. In addition, ethane, a daughter product of CA was detected in composite
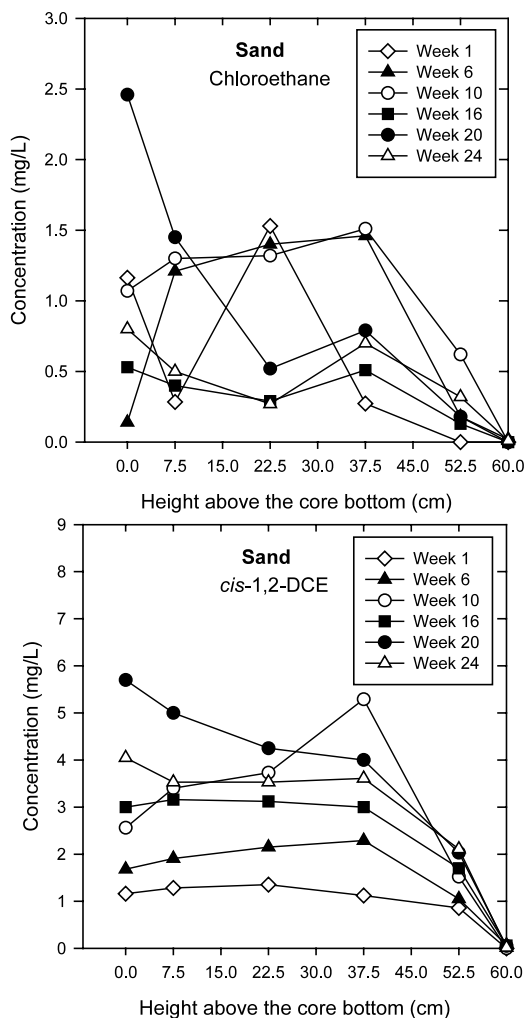
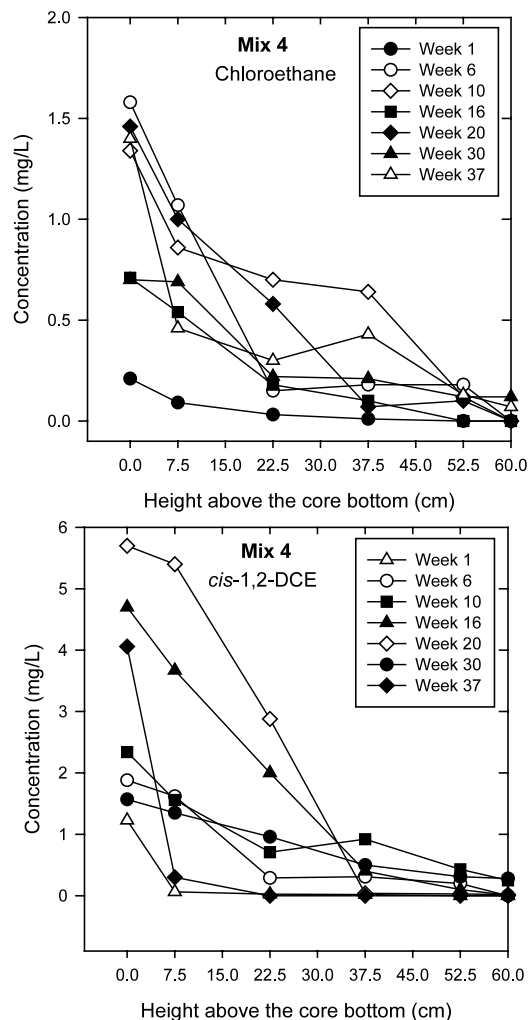Fig. 2. Porewater concentration profiles of *cis*-1,2-DCE and chloroethane in sand core for selected weeks.

Fig. 3. Porewater concentration profiles of *cis*-1,2-DCE and chloroethane in Mix 4 core for selected weeks.

samples collected from the top three sampling ports (data not shown). The appearance of these daughter products was used to identify the onset of biodegradation.

The distribution of *cis*-1,2-DCE and CA in the core containing Mix 7 (peat, sand and compost) is shown in Fig. 5. A similar onset of biodegradation was observed from 10 to 12 weeks after initiating the experiment as seen in Mix 4. *cis*-1,2-DCE was observed to decrease with distance from the inlet whereas concentration of VC (a daughter product of *cis*-1,2-DCE degradation) was noted to in-

crease. Remarkably, by week 12 over 90% of the *cis*-1,2-DCE was degraded to VC between the inlet and the first sampling point, a distance of only 7.5 cm. A representative profile of this trend is presented as Fig. 4. Similar trends were observed for CA in Mix 7 although decreases in concentration were less pronounced. Mass balancing of contaminants in the system was complicated because it was difficult to differentiate between the biodegraded and sorbed fractions of the contaminants.
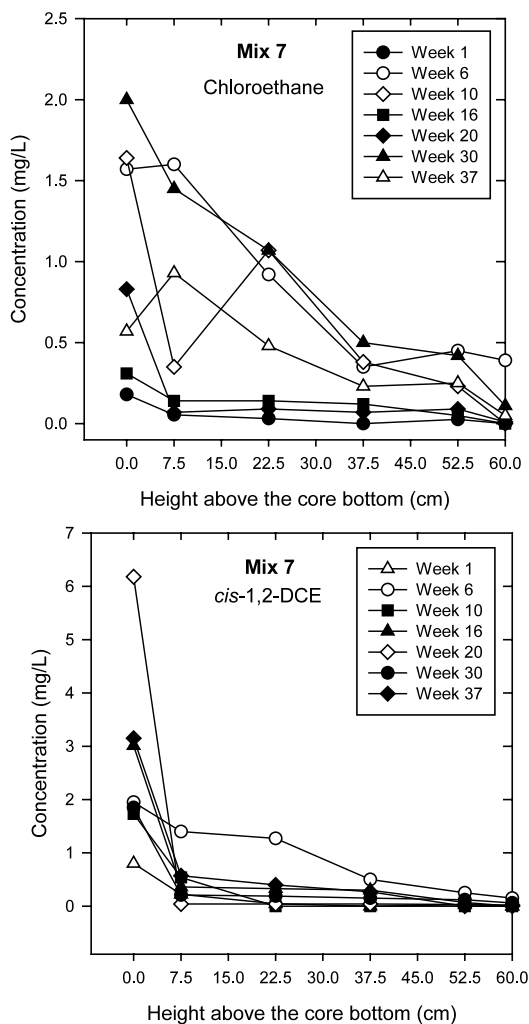
Fig. 4. Sample plots of porewater concentration profiles of *cis*-1,2-DCE and VC in Mix 4 and Mix 7 for week 33.

Fig. 5. Porewater concentration profiles of *cis*-1,2-DCE and chloroethane in Mix 7 core for selected weeks.

Despite the promising evidence of biodegradation, breakthrough of chloroethenes and chloroethanes was observed. Breakthrough of *cis*-1,2-DCE was transient in the mixture containing Latimer peat and sand alone (Mix 4). Once evidence for biodegradation was observed, breakthrough ceased. For the chloroethanes (1,1-DCA and CA), breakthrough occurred for both mixtures even late in the study. Concentrations in the overlying water for these compounds ranged from 0.35 to 2.76 mg/l for CA and from 0.35 to 1.08 mg/l for 1,1-DCA. These concentrations are higher
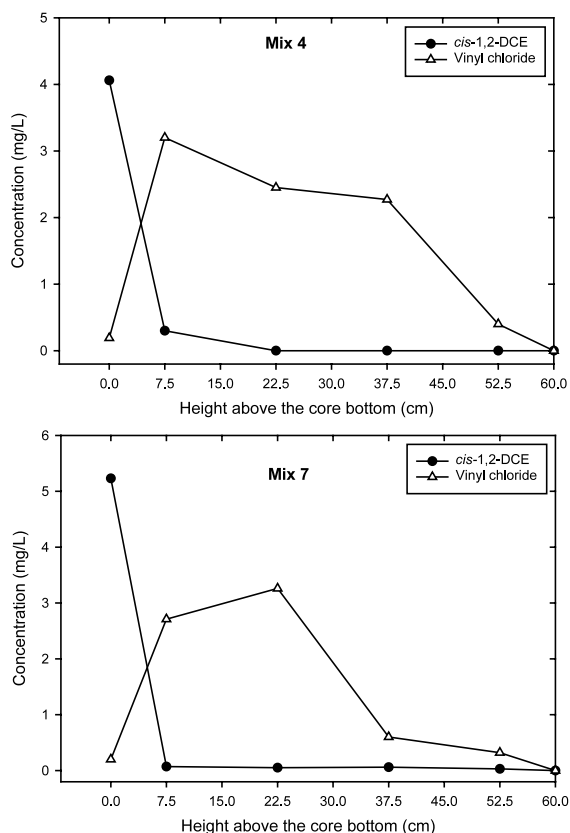
than those observed in the standing water of the sand column probably due to higher volatilization rate in the sand core due to the absence of vegetation cover coupled with higher permeability of sand. This indicates a deeper wetland bed is necessary to fully treat these compounds.

Data for target organics were fit to the first order kinetic reaction equations (Eqs. (8) and (10)). A software package (Table Curve 2D Version 4; SPSS, Inc.) was used to fit data to the degradation equations to determine the lumped temporal and spatial removal rate constants. Removal rate constants were determined from VOC monitoring data collected after contaminant plumes have broken through the columns (for *cis*-1,2-DCE, Mix 4 = 13 days; Mix 7 = 28 days) and the onset of biodegradation, by that time equilibrium was assumed. The VOC data fit reasonably
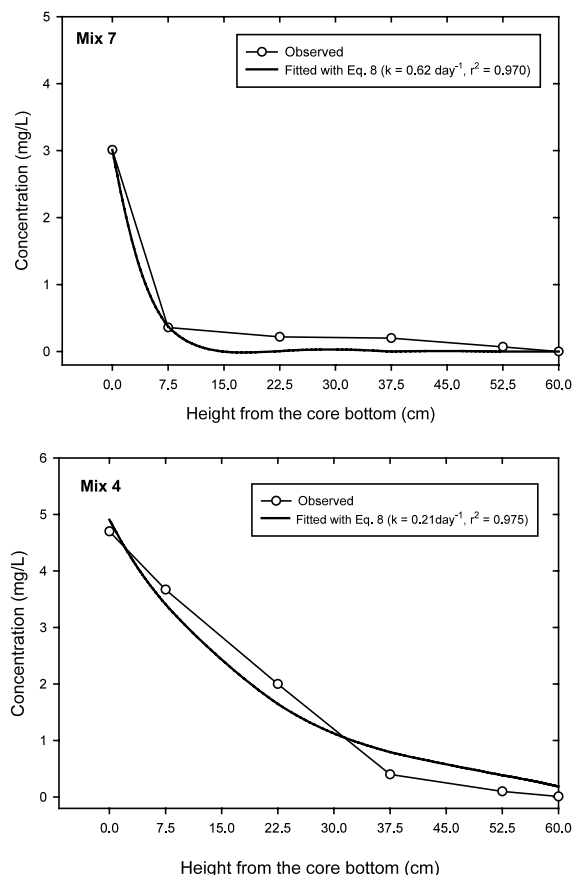
Fig. 6. Experimental data and curve fit of *cis*-1,2-DCE for

well ($r^2 > 0.8$) with the first–order kinetic reaction equation as representative plots in Fig. 6 demonstrate. Table 6 summarizes the removal rate constants. As expected, the degradation rate of chlorinated solvents increased with increasing number of chlorine atoms for both mixes. This observation is consistent with the fact that under anaerobic conditions the more chlorinated aliphatic hydrocarbons are dehalogenated faster than the less chlorinated ones (Fathepure et al., 1997; Haston and McCarty, 1999; Kao and Lei, 2000). It is, however, worth noting that these removal rates may be lower for the actual field conditions since the temperature at which the experiments were conducted (26 °C) are higher than the field temperatures, especially during cold seasons. However, temperature correction coefficients for reductive dechlorination reaction rates are yet to be established. As with other biological reactions, rate constants may decrease by a factor of 2 with every 10 °C drop in temperature.

Mean values of removal rate constants of *cis*-1,2-DCE and 1,1,1-TCA were found to be statistically higher in the Mix 7 column at $\alpha = 0.05$. The measured first order temporal removal rate constants (1/day) for *cis*-1,2-DCE are two orders of magnitude higher than field measurements in aquifers (0.0012–0.0017/day) reported by Wiedemeier et al. (1996). In addition, first-order removal

Table 6
Temporal and spatial removal rate constants

Compound	n	Influent concentration range, C_o		Removal rate constants (26±3 °C)			
		Mix 7	Mix 4	Mix 7		Mix 4	
		(mg/l)	(mg/l)	Temporal (k)[a] (1/day)	Spatial (k_s)[b] (1/cm)	Temporal (k) (1/day)	Spatial (k_s) (1/cm)
cis-1,2 dichloroethene	25	0.85–13.67	1.00–12.40	0.84±0.36	0.41±0.15	0.37±0.13	0.09±0.03
1,1,1-trichloroethane	25	0.02–1.14	0.12–1.08	6.52±3.12	2.80±1.34	1.48±0.42	0.42±0.11

n, Number of observation sets.
[a] Calculated using Eq. (8).
[b] Calculated using Eq. (10).

rate constants of *cis*-1,2-DCE (0.009–0.026/day) and 1,1,1-TCA (0.003–1.73/day) in anaerobic microcosms for various studies reported by Wiedemeier et al. (1999) are much lower than those reported in the present study. Rate constants determined by batch and column experiments are not expected to be the same since batch experiments are conducted under static conditions whereas column experiments are done under advective and dispersive flow conditions similar to those in the field (Porro et al., 2000).

The ability of Mix 7 to degrade *cis*-1,2-DCE and 1,1,1-TCA more efficiently than Mix 4 may be due to several factors. A difference in microbial activity attributed to the presence of the Bion Soil is the likeliest explanation. Mix 7 was capable of supporting plant growth much better than Mix 4. The number of plant stems in the Mix 7 cores after 32 weeks was 136 compared with 31 in the Mix 4 cores. At the end of week 20 plant roots had extended to the bottom of the cores in both soil substrate mixtures.

3.4. Redox conditions in the cores

Results for measurement of temperature, pH, total dissolved solids, ORP and conductivity did not clarify differences in biodegradation rates observed between the cores. Redox potentials for Mix 7 varied between -103 and -80 mV while those in Mix 4 ranged from -175 to -145 mV. These ranges of redox potential suggest that anaerobic reduction of chlorinated solvents in the peat substrate mixtures is feasible (Wiedemeier et al., 1999). Higher TDS (397–2703 mg/l) and conductivity (564–3400 μS) measurements observed in Mix 4 indicate that Bion Soil possesses some salt content.

Composite samples from the root zone and below root zone for analysis of dissolved gases (ethene, ethane, methane and hydrogen) and organic acids were collected three times. Results from the dissolved gas measurements indicate that methanogenic conditions were operating in the columns. Methane concentrations varied across a wide range. Concentrations were near the detection limit of 0.008 mg/l in the root zone of Mix 4 and Mix 7 early in the experiment. The highest

concentrations measured were 0.74 mg/l in Mix 7 and 0.31 mg/l in Mix 4 from composite samples taken from the lower sections of the cores. Methane concentrations were consistently higher in Mix 7. Since reductive dechlorination reactions are most commonly associated with methanogenic conditions, redox conditions in the columns were therefore favorable for degradation of VOCs (Ballapragada et al., 1997). The detection of ethene and ethane, final degradation products of chloroethenes and chloroethanes correlates well with what was observed with the VOCs. Composite samples detected ethene as high as 220 μg/l in Mix 4 and Mix 7 columns. Since the composite samples are subject to dilution, it is expected that actual concentrations were higher. Trace amounts of hydrogen (< 10 μg/l) were detected in pore water samples collected from both Mix 4 and Mix 7 columns. Organic acids were not detected from the analyzed samples at a detection limit of 0.5 mg/l.

3.5. Anaerobic microcosms

Anaerobic microcosms were used to confirm that removal rates were due to anaerobic biodegradation in the lower portion of the bed as demonstrated by the VOC profiles. The mixed cultures were able to degrade 1,2-DCA under anaerobic conditions without a lag, suggesting robust indigenous bacterial populations (Fig. 7).
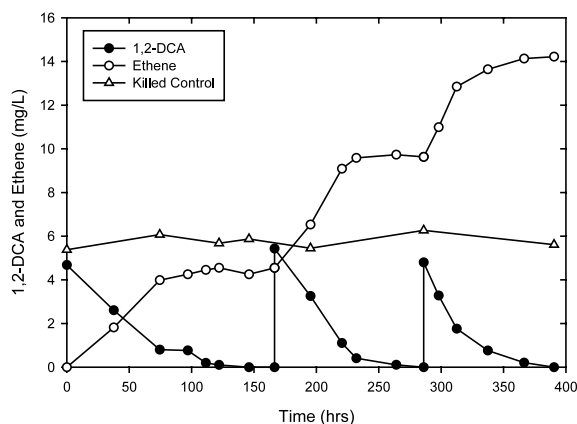

Fig. 7. Temporal trends of 1,2-DCA degradation in anaerobic microcosms of Mix 7.

The redox indicator remained colorless throughout the study demonstrating that low redox conditions were maintained in the microcosms. Ethene was the primary product of degradation since other potential 1,2-DCA possible metabolites (notably VC, CA and ethane) were below the detection limit of the instrument (10 μg/l at these dilutions). 1,2-DCA was therefore dechlorinated mainly to ethene in essentially a single step, reductive dihaloelimination reaction (Klečka et al., 1998). As shown in Fig. 7 anaerobic biodegradation of 1,2-DCA started almost immediately after incubation; no lag period was evident prior to disappearance of the parent compound in all substrate mixtures. After 5 days, over 95% of the parent compound was degraded in the active microcosms of Mix 7, whereas over 90% of the initial 1,2-DCA concentrations were recovered in the killed controls within the same period. In Mix 4 microcosms, the proportion of 1,2-DCA degraded in Mix 4 was 75% for live treatments and 96% was recovered in formalin-amended treatments after 5 days. Detection of ethene coincided with the onset of the disappearance of 1,2-DCA thus suggesting that the formation of ethene was indeed due to biological activity because it was not detected in killed controls. Amounts of ethene quantified in the active microcosms at the end of the incubation period were consistent with the stoichiometric conversion of DCA to ethene.

cis-1,2-DCE degraded almost immediately after incubation without a noticeable lag period (Fig. 8). Degradation of cis-1,2-DCE proceeded with little accumulation of VC. It can furthermore be observed from Fig. 8 that VC conversion to ethene started even before 1,2-cis-DCE was completely depleted, thus suggesting that the mixed cultures could also metabolize VC. Repeated doses of cis-1,2-DCE showed the same trend. Similar DCE degradation trends were also observed in Mix 4, however, the degradation kinetics were slower than in Mix 7. Pseudo first-order degradation rate constants of DCE and DCA in Mix 4 were calculated and found to be 1.1 ± 0.12/day (half life, $t_{1/2} = 0.63 \pm 0.07$ days) and 0.31 ± 0.05/day ($t_{1/2} = 2.2 \pm 0.34$ days), respectively. In contrast, degradation rate constants of DCE and DCA in Mix 7 were respectively 1.7 ± 0.19/day ($t_{1/2} = 0.41 \pm 0.05$ days) and 0.77 ± 0.18/day ($t_{1/2} = 0.90 \pm 0.14$ days).

Degradation rate constants of VC were determined using Eq. (12) using a software package Sigma Plot 6.0 (SPSS Inc., Chicago, IL), which employs a Marquardt–Levenberg algorithm to find the parameters of interest from the observed data. Degradation rate constants of VC in Mix 4 and Mix 7 were found to be 0.59 ± 0.15/day ($t_{1/2} = 1.17 \pm 0.31$ days) and 1.12 ± 0.22/day ($t_{1/2} = 0.62 \pm 0.13$ days), respectively. Differences in degradation rate constants in Mix 4 and Mix 7 were found to be statistically significant ($\alpha = 0.05$) for all test compounds. Therefore, results of microcosm experiments confirmed the observations made during the column studies that Mix 7 was more effective in attenuation of the target compounds than Mix 4. It can also be inferred from the results of degradation kinetic studies of the test compounds in the microcosms that biodegradation was probably the most important removal mechanism of VOCs in the mesocosms when compared with sorption, plant uptake and volatilization. Degradation rate constants for cis-1,2-DCE in the microcosms are at least higher by a factor of two than those observed in soil columns. This may be due to lack of mass transfer limitations in the more homogeneous microcosms.
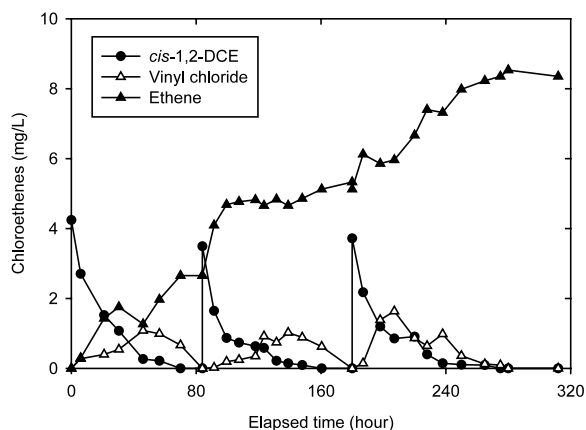

Fig. 8. Temporal trends of cis-1,2-DCE in anaerobic microcosms of Mix 7.

3.6. Wetland bed depth

Based on the findings of the study, effective wetland bed depths required to meet National Primary Drinking Water Regulations (NPDWRs) (EPA, 2002) of cis-1,2-DCE (70 μg/l), VC (2 μg/l) and that of 1,1,1-TCA (200 μg/l) for different scenarios were calculated using the first-order mass transport equation (Eq. (8)). Calculations were based on removal rate constants at 25 °C (temperature at which the studies were conducted) and 15 °C (typical temperature of groundwater at the Superfund site during cold seasons).

For calculating the wetland depth, removal rate constants observed in the soil columns were halved to account for a decrease in microbially mediated degradation reactions in the wetland bed as a result of temperature drop during cold seasons. Since VC is a proven carcinogen, the effective depth required for its removal was also calculated based on the following assumptions: (1) removal rate constants of VC in the soil columns are half those determined in anaerobic microcosms since removal rate constants of cis-1,2-DCE in soil columns were approximately half those found in anaerobic microcosms; (2) removal rate constants during cold seasons (groundwater temperature 15 °C) are lower by a factor of two than those observed in column studies (26 °C); and, (3) cis-1,2-DCE is stoichiometrically transformed into VC at the bottom immediately after entering the wetland. The calculations assumed a loading of 15 gpm/acre, about half of the critical flow for both substrate mixtures and the loading utilized in laboratory testing to minimize chances of bed fluidization. The wetland bed depth calculation results are summarized in Table 7.

Table 7 demonstrates that for all scenarios and contaminants, wetland beds constructed from the mixture containing peat, compost and sand (Mix 7) will be shallower and most likely more cost-effective than the ones constructed from peat and sand alone (Mix 4). For this groundwater composition, VC appears to be the design contaminant, requiring more bed depth to remove observed contaminants to meet the NPDWRs. The combined stimulation of the removal rate and the retardation coefficient by the addition of the compost material argues strongly for a peat-compost-sand recipe for the upflow treatment wetland.

4. Conclusion

The present study has attempted to address some unknown aspects of the treatment wetland-VOC concept including determination of sorption potential of the candidate sand/peat/compost mixtures, degradation kinetic reaction rates of target contaminants within the bed, the lag time for degradation to begin after system start-up and the hydrodynamic behavior of the peat bed. Other unknowns include the actual field degradation rates and the seasonally and spatial variability of degradation processes due primarily to weather changes (especially temperature and precipitation).

Table 7
Effective wetland bed depths to required meet MCL of VOCs for different scenarios

Compound	Maximum concentration, C_o	Removal rate constant (26 °C)	R	Effective wetland bed depth[a] (cm)	
	(mg/l)	(1/day)		26 °C	15 °C
Mix 7 (Peat:sand:compost)					
cis-1,2-DCE	13.67	0.84	7.32	7	14
VC	13.67	0.56	1.20	105	210
Mix 4 (Latimer:sand)					
cis-1,2-DCE	13.67	0.37	3.51	35	70
VC	13.67	0.30	1.07	250	900

[a] Calculated using Eq. (8). NPDWRs' maximum concentration level of cis-1,2-DCE and VC are respectively 70 and 2 μg/l. Design flow of the treatment wetland system is 15 gpm/acre (160 l/min/ha).

These latter questions will only be answered in the pilot study itself because the present work was not meant to replicate a well-developed treatment wetland and did not mimic actual field conditions. However, the present study has shed light on some potential design, construction and operational problems that may be encountered in the process of developing the treatment wetland concept into a full-scale groundwater treatment system for chlorinated solvents. For example, breakthrough of some target compounds (especially chloroethanes) may occur in the pilot plant during system start-up as it did during the bench-scale studies and this problem needs to be properly addressed in the design of the pilot system and eventually in the full-scale treatment system. Notwithstanding the observed limitations of the study, results from the present work have suggested that treatment wetland may potentially be a technically and economically viable option for treatment of groundwater contaminated with chlorinated solvents.

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